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Thermodynamics of solvation and solvophobic effect in formamide

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ABSTRACT

Using semi-adiabatic calorimetry, we measured the enthalpies of solution for various low-polar compounds including alkanes, aromatic hydrocarbons and their halogenated derivatives in formamide at temperature of 298 K. For the same compounds, the values of limiting activity coefficients in formamide were determined using GC headspace analysis at 298 K, and Gibbs free energies of solution and solvation were calculated. Based on these data and the available literature values of the Gibbs free energy of solvation in formamide for a number of other low-polar solutes, a study of the solvophobic effect in this solvent is performed, and its resemblance to the hydrophobic effect in aqueous solutions is demonstrated. It is shown that the contribution of the solvophobic effect into the solvation Gibbs free energy in formamide is much higher than that in aliphatic alcohols, but lower than that in water. Like in water, the magnitude of this contribution for different solutes linearly increases with the solute molecular volume. Solvophobic effect also significantly affects the enthalpies of dissolution in formamide, causing them to be more negative in the case of alkanes and more positive in the case of arenes.

1. Introduction

Formamide $HCONH_2$ is an important solvent from both practical and theoretical points of view. Formamide finds its applications as a solvent in life science and technology and is promising for green organic synthesis. It is used in hybridization solutions for hybridization of nucleic acid duplexes [1] and as a component of cryoprotectant mixtures for vitrification of tissues [2]. In liquid formamide, its molecules form strong intermolecular hydrogen bonds [3]. Interest in the structural and energetic characteristics of these bonds shown by a number of researchers is due both to the fact that formamide is the simplest compound containing –CO–NH– fragment, which is present in peptides and proteins, and some analogy between hydrogen bond networks in formamide and liquid water [3–5]. Hydrogen bonds in water play a huge role in many natural phenomena and processes, and formamide is sometimes considered as an alternative solvent to water that is able to support life with some alternative biochemistry [6].

The similarity of formamide and water is quite obvious, if we consider the solubilities of various compounds. Non-polar substances have low solubility and high values of Gibbs free energy of dissolution in both solvents, while polar organic solutes and many inorganic salts are well soluble in water and formamide. Additionally, micelles can form in formamide solutions from the same amphiphilic surfactant molecules that form micelles in water, however, in formamide this process takes place at higher concentrations of surfactants [7].

2. Methodology

2.1. Solvophobic effect in formamide and thermodynamic functions of solution

An evident similarity in thermodynamic properties of aqueous solutions and solutions in formamide and in a number of other self-associated solvents led to introduction of the concept of solvophobic effects [8], by analogy with the hydrophobic effect. These effects influence thermodynamic and other properties of solutions in self-associated solvents. However, this concept remained fairly vague for a long time: no strict definition and no criterion to judge whether the solvophobic effect takes place in a certain system or not. In a recent paper [9], we proposed to recognize the presence of the solvophobic effects in solutions by considering the relationship between the Gibbs free energies and enthalpies of solvation. According to this approach and available experimental data, in formamide solutions the solvophobic effect is very strong, although weaker than in water. However, there is not enough literature values of the thermodynamic functions of solvation to quantify the solvophobic effect in formamide. Above all, the enthalpies of dissolution of low-polar compounds in formamide are unknown or unreliable.

Measurement of the enthalpy of dissolution of low-polar substances in formamide is difficult because of their low solubility, low dissolution rate, and high viscosity of solvent. Even under

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